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EXPLORATORY DEVELOPMENT OF FOAMS FROM
LIQUID CRYSTAL POLYMERS

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FOREWORD

This report was prepared by personnel of Celanese Research Company under contract NAS1-17290. The work was administered under the direction of the National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia. The assistance of Dr. Vernon Bell and Ms. Ann Timberlake of NASA is acknowledged.

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I. ABSTRACT

Two types of liquid crystal polymer (LCP) compositions were studied and evaluated as structural foam materials. One is a copolymer of 6-hydroxy-2-naphthoic acid, terephthalic acid, and p-acetoxyacetanilide (designated HNA/TA/AAA), and the other is a copolymer of p-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid (designated HBA/HNA).

Experimental results show that the extruded HNA/TA/AAA foams have better mechanical quality and appearance than HBA/HNA foams. Heat treatment improves foam tensile strength and break elongation, but reduces their modulus. The injection molding results indicate that nitrogen foaming agents with a low-pressure process give better void distribution in the injection molded LCP foams than those made by the conventional injection-molding machine and chemical blowing agents. However, in comparing LCP foams with other conventional plastic foams, HBA/HNA foams have better mechanical properties than foamed ABS and PS, but are comparable to PBT and inferior to polycarbonate foams, especially in heat-deflection temperature and impact resistance energy. These deficiencies are due to LCP molecules not having been fully oriented during the Union-Carbide low-pressure foaming process.

II. INTRODUCTION

Polymeric foams are materials with a unique combination of properties. They consist of a polymeric matrix with gas enclosures. These materials have the ability to insulate heat, sound, and vibration. Recently, they have become one of the important engineering materials to absorb impact energy for protecting automobiles and electronic equipment. Because of their unique stress-strain properties, they are also capable of distributing the impact forces evenly over the surface of an impactor. Applications of structure foams for military end uses, such as an interior support for helmets, have been identified.

Usually, there are three types of polymeric foam systems: (1) a thermoplastic foam, which is formed by gas bubbles created by nitrogen or chemical blow agents dispersed in the melt; (2) a thermoset foam, in which the polymeric matrix is a thermosetting material; and (3) a system in which cellular structures are generated by removing a fugitive phase from a polymeric matrix.

Approximately 90% of structural foam products are fabricated by molding process¹. The remaining 10% are processed by the extrusion process. Basically, there are three types of molding processes, namely: the Union-Carbide low-pressure process²; the USM high-pressure process³; and the conventional injection-molding process. The Union-Carbide low-pressure process is the most frequently used today to produce structural foams. Basic equipment consists of an extruder, a valve, a hydraulic accumulator, a high-pressure gas supply, and a mold. During operation, resin is melted in the extruder barrel and mixed with an inert gas, usually nitrogen, forced into the accumulator and held there under pressure. When the correct shot size has been retained in the accumulator, the nozzle valve is opened and the plastic and gas mixture are forced into the mold. The melt is expanded in

the mold by the pressurized gas until the mold is completely filled. Organic blowing agents can be pre-mixed with the resin and used for foaming instead of the inert gas. Due to the low molding pressure and flow rate, parts molded by this process have low residual stresses. The main drawback of the process is that the finished products have swirl patterns on the surface. Polishing and painting are, therefore, necessary for molded products.

The uniqueness of the USM high-pressure process is the employment of an expandable mold. In other words, the mold is first filled with a foamable melt, and then foaming is allowed to proceed as one of the mold halves expands. As a result, molded parts have better surface quality and uniformity than those made by the Union-Carbide process. However, more distinct skin and core structure is created by this high-pressure approach. The main limitation of this process is that parts have to be simple or flat so that molds are able to expand during the process.

If foams are made by the conventional injection-molding machine, chemical blowing agents are used. Similar to the low-pressure process, a "short shot" method is employed. Because it uses higher injection pressure and speed than the Union-Carbide low-pressure process, and also because melt and blowing agents have much shorter residence time in the barrel, process control for the bubble growth during this process is very complicated. Samples fabricated by the conventional injection-molding approach generally have a poor void distribution.

Extruded foam products are usually produced by the conventional extrusion process with chemical or nitrogen blowing agents. If a chemical blowing agent is used, a pre-blend of polymer and blowing agent is fed into the extruder, where plastification and decomposition of the blowing agent occur under high-pressure in order to prevent any premature inflation before the melt leaves the die. Therefore, temperature profile along the

extruder is kept low except near the die of the extruder. If physical blowing agents are employed, the gas is injected through one or more orifices in the cylinder by means of a precisely controlled piston. The polymer should be heated as much as possible to reduce its viscosity prior to blowing agent injection in order to facilitate its dispersion. The foaming extrudate expands as it emerges from the die, and then is solidified and pulled by a take-up device.

Since the main end uses of most thermoplastic foams are furniture and building and construction applications, the requirements for a polymer to be a structural foam matrix are simple. In order to explore the feasibility of using structural foams at high temperature and under severe environmental conditions, a polymer with good chemical resistance and stability is needed. In recent years, Celanese has developed a new class of polymeric materials based on hydroxynaphthoic acid chemistry, consisting of rigid backbone molecules. These polymers exhibit liquid crystalline order in the melt, which produces a high degree of molecular orientation and excellent mechanical properties. Unlike lyotropic liquid crystal polymers, thermotropic liquid crystal polymers can be easily processed using conventional injection-molding or extrusion equipment.

Articles fabricated from LCP materials have shown mechanical properties generally superior to conventional fiber-reinforced engineering resins. Solvent resistance, as well as dimensional stability, are also generally superior to conventional thermoplastic resins. Due to the unique mechanical properties and excellent chemical resistance, it is anticipated that these LCP materials will offer advantages as thermoplastic foam resins. Work related to fabrication techniques and mechanical properties of LCP foams is documented in this report.

III. LITERATURE SURVEY

1. Bubble Formation and Growth: Studies of structural foams can be divided into two areas, namely: bubble formation and growth and mechanical properties of foams. Since a blowing agent is dissolved in a molten polymer, bubbles have to nucleate from the molten polymer and grow by diffusion of a blowing agent from the molten polymer to the nucleated gas bubbles. Hansen and co-workers^{4,5,6} have found that fillers (i.e., metal particles, sodium aluminum silicate, SiO_2 , Fe_2O_3) perform as nucleating sites for the formation of bubbles from the dissolved gas. They suggested that uniform and small cell structure was obtained in an extrusion process only when decomposition of the blowing agent was not complete within the extruder. As a result, pressure in the head and die of the extruder must be equal to or greater than that required to keep dissolved gas in the solution.

Once the nucleated bubbles reach a certain minimum size, they will continue to expand until the pressure within them is equal to the external pressure in the melt. Epstein and Plesset⁷ analyzed the diffusion controlled growth of a stationary gas bubble suspended in a Newtonian fluid; they obtained the following equation to describe the bubble growth:

$$R(t) = kt^{1/2} \quad (1)$$

where R is the bubble radius, t is the time, and k is a rate constant which is a function of diffusion coefficient, solubility of gas in the fluid, as well as the initial concentration of gas in the fluid. Experimental results reported by Gent and Tompkins⁸ and Stewart⁹ showed good agreement with the above equation.

Studying a single bubble growth in a stationary molten polymer, Villamizar and Han¹⁰ found that Equation (1) should be revised as:

$$R(t) = kt^n \quad (2)$$

in which n increases with an increase in temperature. This is due to the fact that an increase in melt temperature results in a decrease in melt viscosity. Hobbs¹¹ extended the Epstein-Plesset theory by incorporating the kinetics of coalescence of small bubbles into the calculation. The effect of melt viscosity on bubble growth was also studied by Yang and Yeh¹² as well as Street et al.¹³. The following conclusions can be drawn from their analyses: (1) bubbles grow faster in an isothermal condition than in a non-isothermal case; (2) in non-Newtonian fluids, a bubble has a greater growth rate than in a Newtonian fluid; and (3) the diffusivity and concentration of blow agents are the most important parameters influencing the bubble growth. Street¹⁴, Zana and Lead¹⁵, and Fogler and Goddard¹⁶ included the viscoelastic force into the calculations. They showed that, for very large values of Henry's law constant, the rate of bubble growth is mainly controlled by fluid rheology rather than by mass transfer rate. However, for very small values of the constant, the bubble growth rate may be completely controlled by the diffusion process. In addition, they found that the melt viscoelastic character can inhibit bubble growth during the end of growth.

Han and co-workers^{17,18} conducted visual observations of the dynamic bubble growth behavior. They found that bubbles start to grow when the pressure within the extruder die is below a critical pressure. Experimental results indicated that this critical pressure decreases with increasing melt temperature and increases with an increase in the blow agent concentration. Throne¹⁹ explained this critical pressure-temperature relationship using a Henry's law model. Han and Yoo²⁰ also simulated a single bubble growth in a rectangular injection mold cavity. Using an isothermal assumption, they found that: (1) the initial growth rate of the bubble is retarded if the injection pressure is increased; (2) the melt elasticity appears to enhance the

initial bubble growth rate; (3) the rate of bubble growth is decreased as the melt viscosity increases; and (4) an increase in blowing agent concentration and diffusion coefficient results in a fast bubble growth rate.

2. Structure-Property Relationships: Meinecke and Clark²¹, Throne²², and Wendle²³ have given thorough reviews on structure-property relationships for structural foams. Fundamental studies on Young's modulus retention as a function of void content have received the most attention. Gent and Thomas^{24,25} developed a first simple model to describe the Young's modulus of a foam, E_f , to the volume fraction of void content, x , in a foam, as follows:

$$\frac{E_f}{E} = \frac{\beta^2}{2(1+\beta)} \quad (3)$$

and

$$1-x = 3\beta^2 + \frac{\beta^3}{(1+\beta)^3} \quad (4)$$

This model has been found to be in agreement with the published experimental data for polyurethane foams²⁷. However, a deficiency of this model is that it cannot correctly predict the modulus of high-density foams. Rusch²⁸ modified this model, and proposed the following equation:

$$\frac{E_f}{E} = x (2 + 7x + 3x^2)/12 \quad (5)$$

Han²⁹ proposed a simple empirical equation which fits most published data:

$$\frac{E_f}{E} = (1-x)^2 \quad (6)$$

Throne³⁰ reported that the best data fit for the tensile strength, T_f , of thermoplastic foam is:

$$\frac{T_f}{T} = (1-x)^2 \quad (7)$$

where T is the tensile strength of solid samples.

Throne²² further proposed a similar equation for the flexural modulus retention:

$$\frac{M_f}{M} = (1-x)^2 \quad (8)$$

where M_f and M are the flexural moduli of the foam and the control, respectively. However, Meinecke and Clark²¹ found that this equation seems to give only a lower bound. Egli³¹ suggested a $3/2$ power relationship:

$$\frac{M_f}{M} = (1-x)^{3/2} \quad (9)$$

Throne³⁰ also derived some tentative equations for the impact, creep, and fatigue behavior of foams.

3. Liquid Crystal Polymers: With regard to liquid crystal polymers, researchers at Tennessee Eastman were among the first to publish the preparation, viscosity behavior, and mechanical properties of liquid crystal polymers 32-36. The materials used in their studies were derived from the acidolysis reaction of polyethylene terephthalate (PET) and a variety of dicarboxylic acids and acetylated difunctional phenols. Some of these polymers have turbid melts, unusual melt viscosity behavior, and gave unusually anisotropic molded articles showing liquid crystalline behaviors. Since then, a considerable number of studies have been reported in the literature. In general, they can be divided

into three categories: (1) formation and chemical structure of liquid crystal polymers; (2) rheological behaviors; and (3) processing and applications.

Smith³⁷ compared the basic differences between low molecular weight liquid crystals and liquid crystal polymers. He summarized the orientation behavior and physical properties of liquid crystal polymers from previous reviews and literature. White and Fellers³⁸ and Samulski and DuPré³⁹ reviewed the formation and chemical structure of macromolecular liquid crystals which form fibers with unusually high levels of orientation and strength. Lenz and his coworkers⁴⁰ gave a thorough review of the previous studies on the synthesis of thermotropic liquid crystalline polyesters. They discussed and investigated the advantages of using flexible, semi-flexible, and non-mesogenic spacer groups in liquid crystal polymers for suppressing the melting points below their decomposition temperatures. Jackson⁴¹ also studied the effect of polymer structure on the melting points and mechanical properties of liquid crystalline aromatic polyesters. Krigbaum et al.⁴² investigated the effect of the number of methylene units in thermotropic polyesters. Calundann and Jaffe⁴³ summarized the recent industrial developments of anisotropic polymers from their theoretical origins and synthesis through the fabrication of fiber and film. The effects of polymer composition on the chemical and physical properties of final products were discussed in detail.

The rheology of low molecular weight liquid crystalline materials was reviewed in 1967 by Porter and Johnson⁴⁴. In 1978, Baird⁴⁵ reviewed liquid crystal polymer rheological behavior. In 1981, Wissbrun⁴⁶ gave a more in-depth and thorough review of this subject based on the three-region flow curve proposed by Onogi and Asada⁴⁷. In general, the shear viscosity of liquid crystal polymers is much lower than that of conventional polymers at a comparable molecular weight. The relaxation time

and elasticity of liquid crystal polymers are greater than those of isotropic polymers. In addition, liquid crystal polymers often show a variety of phenomena which are not seen with isotropic polymers, including the observation of negative first normal stress difference^{48,49}, regions of shear thickening viscosity, and a secondary maximum in transient shear flow^{50,51}. Due to this strange flow behavior, it was anticipated that molding liquid crystal polymeric foams would be quite different from the conventional ones.

Compared to the studies of formation and rheology of thermotropic liquid crystal polymers, relatively little work has been published in the area of liquid crystal polymer processing. McFarlane and coworkers³²⁻³⁶ reported that the tensile strength of the molded thin liquid crystal polymer bars was four or five times stronger than those obtained from conventional polymers due to flow-induced orientation. Ide and Ophir⁵² studied the influence of shear and elongational flows on the orientation development in wholly aromatic thermotropic copolyesters. They observed extremely dominant orientation effects due to elongational flow. Acierno et al.⁵³, in the study of orientation buildup in thermotropic polyester fibers, found that semi-flexible polyesters that form a thermotropic nematic phase generally exhibit lower crystallinity and poorer crystal perfection than those forming smectic phases. Similar observations of the effects of polymer composition and elongational flow on liquid crystal polymer fiber mechanical properties have been reported by Calundann and Jaffe⁴³. Baird and Wilkes⁵⁴ investigated the factors affecting the formation of skin-core structure. Ophir and Ide⁵⁵ gave a more detailed study of layer structure of liquid crystal molded bars. The effects of various flow fields including fountain, shear, converging and radial flow on the orientation of liquid crystal polymer molecules were discussed.

However, no publication on liquid crystal polymer foams has been reported. Due to the unique melt behavior and the mechanical properties of liquid crystal polymers, it appeared worthwhile to determine the fundamental behavior and properties of this unique, all aromatic liquid crystalline polyester in the cellular state, and to evaluate, in a preliminary manner, the potential for converting these unique materials to useful forms of very low density, high strength foamed aerospace structural materials.

IV. EXPERIMENTAL

1. Polymer Formation and Melt Characterization: The thermoplastic resins studied in this report are two of the Celanese-developed thermotropic liquid crystal polymers (LCP). These resins combine excellent solvent resistance and mechanical property retention over a wide range of temperatures. The two resins are a copolymer of 6-hydroxy-2-naphthoic acid (60%), terephthalic acid (20%) and p-acetoxyacetanilide (20%) (designated HNA/TA/AAA 60/20/20), and a copolymer of p-hydroxybenzoic acid (73%) and 6-hydroxy-2-naphthoic acid (27%) (designated HBA/HNA 73/27). The details of their polymerization conditions were described in the patents^{56,57}.

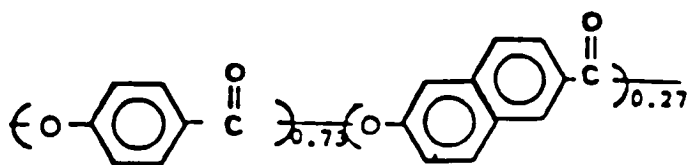
Figure 1 shows their chemical structures. They exhibit ordered structure in the melt, as indicated by birefringent optical properties. Figure 2 demonstrates a typical melting curve of a liquid crystal polymer, as determined by differential scanning calorimetry using a 20°C/min heat-up rate. These polymers have an inherent viscosity in perfluorophenol of approximately 4.5-5 dL/g. Figure 3 shows the melt viscosity as a function of shear rate. These polymers have much lower viscosity than most of the conventional thermoplastic polymers.

2. Blowing Agents: Nitrogen was used as a physical blowing agent, while Celogen® HT550 and Kemtec® 500 were used as chemical blowing agents. The physical blowing agent was injected

Polymer Name

Chemical Structure

HBA/HNA
(73/27)



HNA/TA/AAA
(60/20/20)

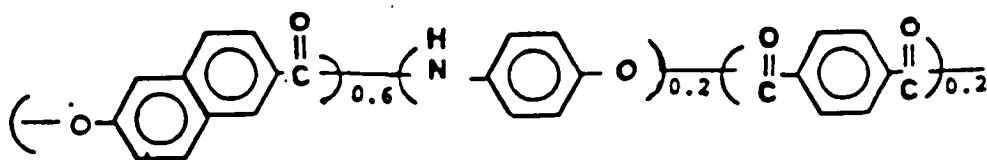


FIGURE 1. CHEMICAL STRUCTURE OF LIQUID CRYSTAL POLYMERS

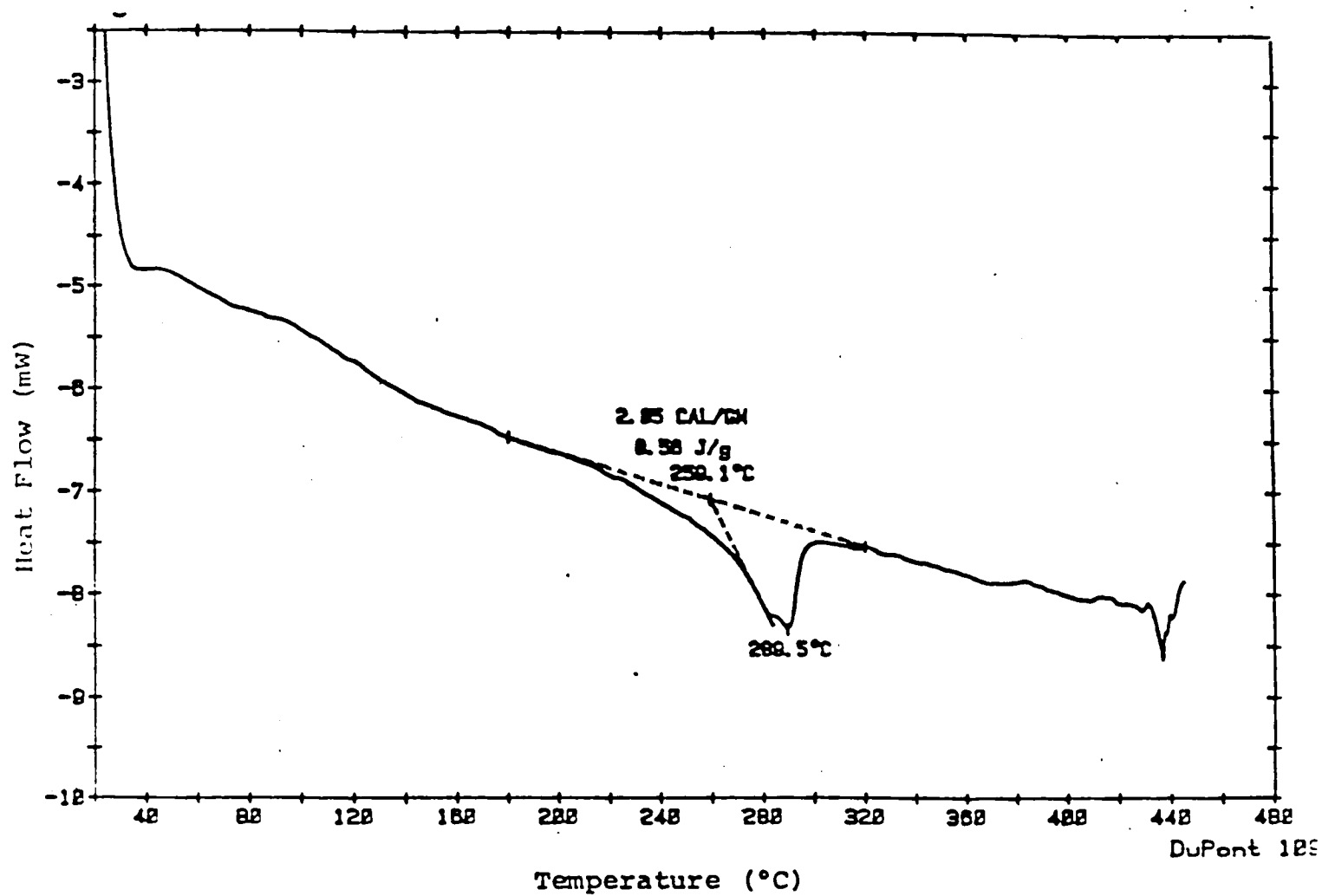


FIGURE 2. THE DSC CURVES OF HNA/TA/AAA POLYMERS

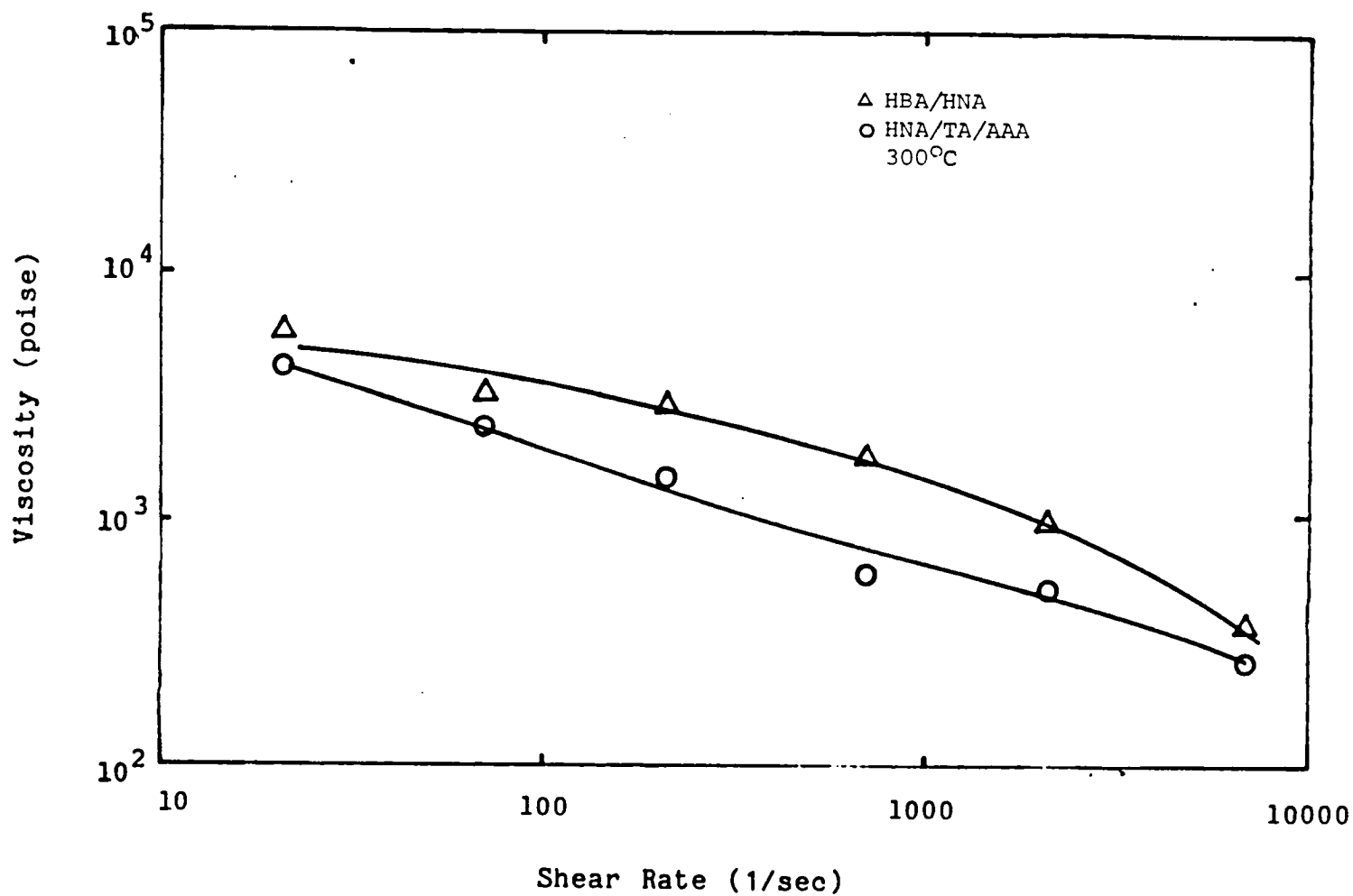


FIGURE 3. MELT VISCOSITY OF LIQUID CRYSTAL POLYMERS

into the hot molten polymer near the end of the screw barrel, whereas the chemical blowing agents were preblended with polymers and 5% Wollastonite, and then added to the hopper of the processing equipment as raw materials for extrusion and injection molding. Wollastonite was used here as a nucleant of gas bubbles.

Table 1 shows the chemical properties of the chemical blowing agents. Both Celogen® HT550 and Kemtec® 500 have proper operational temperatures for our liquid crystal polymers. The main decomposition product is CO₂.

3. Fabrication Approach: Two approaches were used to fabricate liquid crystal polymer foams; namely, extrusion and injection molding. The Brabender extruder was used to produce rods and sheets. The temperature profiles from feeder to die head were 210±20, 245±20, 270±20, and 285±20°C. After being extruded from the die, the rod was immediately cooled down in a water bath so that no further change in diameter occurred, while the sheet was pulled and cooled down on a conveyor belt. The draw down ratio was controlled by the speed of a take-up unit or a moving belt. Calendering was also used as a take-up unit, but failed because the extruded sheets have poor quality due to the tremendous shear and normal stresses imposed on them.

Injection molded articles were produced by a conventional injection molding machine, as well as by the Union Carbide low-pressure process. The conventional molding process used in this

Celogen 550 is a manufacturer's trade mark of the Uniroyal Chemical Company. Kemtec 500 is a manufacturer's trade mark of the Sherwin Williams Co.

The Windsor Injection Machine was produced by Klockner Windsor Company in Germany. The Brabender extruder was produced by the C. W. Brabender, Inc., U.S.A.

TABLE 1. BLOWING AGENTS

	CELOGEN HT550 <u>(Uniroyal)</u>	KEMTEC 500 <u>(Sherwin Williams)</u>
Decomposition Range	271-310°C	235-240°C
Operation Temperature	288-344°C	271-327°C
Decomposition Products	CO ₂ Propylene Isopropylene N ₂ Methane 4-Amino Urazole	CO ₂ CO Nitrogen Oxides
Density	1.178 (g/cc)	1.52 (g/cc)
Use	For polymers that readily undergo chemical degradation	Polyester Polymers

study was an in-house 80-ton reciprocating Windsor® injection molding machine. There are three temperature-control zones along the barrel, and one additional heater band around the nozzle. The temperature setup during these experiments was between 280-300°C along the barrel and 280°C at the nozzle. A shut-off valve was installed within the nozzle in order to prevent molten polymer from drooling. The mold temperature was maintained at 100-120°C by a circulated hot-oil heater. The injection pressure was about 33.5 MPa (4800 psi); the screw rotational speed was 220 rpm. No back pressure was applied on polymers during these trials. The mold had two cavities; one for tensile specimens and the other for flexural samples. Their dimensions conform to ASTM D-638 and 790. The overall cycle time was between 30-60 seconds. Only chemical blowing agent compounded LCP variants were used in this process. The total amount of materials flowing into the cavities was controlled by the short-shot technique. A small amount of melt was injected into the cavity under high pressure and allowed to fill up the mold cavities due to the expansion of bubbles chemically created within the molten polymers.

A nitrogen blowing agent was used in the Union-Carbide process. A $L/D = 30$, 5.08 cm (2-inch) diameter screw extruder was employed to convey the molten polymer to an accumulator which had a capacity of 1.3-9 Kg (3-20 lbs). The temperature profile along the extruder was 160, 232, 260, and 300°C. The pressure within the extruder was around 1.72×10^7 N/m² (2500 psi). Nitrogen was injected into the extruder at a pressure of 1.89×10^7 N/m² (2700 psi). The temperature of the pipe, which was located between the extruder and the accumulator, was kept at 310°C. The temperature and pressure of the accumulator were monitored at 310°C and 1.82×10^7 N/m² (2600 psi), respectively. The mold size was 33 x 24.8 x 0.32 cm³ (13 x 9.75 x 0.25 in³). The mold temperature was maintained at 80-100°C by a circulated hot-oil heater. The overall cycle time was 2.5 minutes.

4. Measurement: We used ASTM D-1622 and buoyancy methods for density measurement, ASTM D-638 and D-1623 for tensile properties, and D-790 for flexural properties. Compressive properties were measured according to ASTM D-1621. The heat deflection temperature of foams was determined according to ASTM D-648 with a load of 1862 KPa (264 psi). Izod notch impact tests were carried out using ASTM D-256. A DuPont 990 thermal analyzer and a model 1942 DuPont thermal mechanical analyzer were used for the measurement of the thermal expansion coefficient.

The orientation of the liquid crystal polymer in the structural foams was examined using X-ray diffraction. Diffraction patterns were recorded photographically using nickel filter CuK^α radiation with the incident beam aligned perpendicular to the machine direction. Orientational parameters were computed from digitized azimuthal microdensitometer scans of the $\langle 110 \rangle$ liquid crystal polymer reflection, which occur in a plane perpendicular to the molecular axis. Herman's orientation functions were calculated assuming uniaxial orientation from the strong equatorial reflection for the liquid crystalline polymer component.

V. RESULTS AND DISCUSSION

1. Extruded Foams:

a. The Effect of Chemical Blowing Agents: Table 2 summarizes the effect of blowing agents on foam properties and shows that both tensile strength and modulus are roughly independent of the chemical composition of blowing agents. In other words, foam properties were dominated by the void contents. This result is in agreement with the experimental observation reported by Han²⁹ and Throne³⁰.

TABLE 2. THE EFFECT OF CHEMICAL BLOWING AGENTS ON SHEET PROPERTIES⁽¹⁾

	Void Content (%)	AS EXTRUDED		HEAT TREATED	
		Tensile Strength/Modulus		Tensile Strength/Modulus	
		MPa/GPa	(Ksi/Msi)	MPa/GPa	(Ksi/Msi)
0.3% Kemtec + HBA/HNA + 1.1% Wollastonite	34	36.6/1.89	(5.24/0.27)	53.5/2.31	(7.65/0.33)
0.3% Celogen + HBA/HNA + 1.1% Wollastonite	36	35.8/2.10	(5.13/0.30)	52.6/2.52	(7.53/0.36)

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(1) 42 mil, Draw-Down Ratio = 1.7-2.0

b. Rod Foams: Figure 4 shows the moduli of HBA/HNA and HNA/TA/AAA rod change with void content. HNA/TA/AAA polymer has a higher modulus than HBA/HNA polymer if the void content is less than 33%. However, a comparison of the slopes of these two polymers shows that HBA/HNA polymer has better mechanical property retention as a function of void content.

Figure 5 illustrates the morphology of these foam rods. Voids distribute more uniformly in HNA/TA/AAA polymer than in HBA/HNA polymer. The HNA/TA/AAA rod has a smooth circumference, while the HBA/HNA rod has an irregular surface. These differences may be due to their difference in melt rheology. In other words, HNA/TA/AAA polymer would appear to have an elongational thickening character, while HBA/HNA melt follows an elongational thinning behavior. Therefore, the former has a higher melt strength than the latter during the expansion of a bubble.

Table 3 summarizes the results of X-ray measurement, and shows that the orientation angles of both polymers decrease and broaden due to the effect of void content during the process.

c. Sheet Foams: Figures 6 and 7 show the tensile strengths of extruded liquid crystal polymer foams as a function of void content. Tables 4 and 5 summarize their tensile properties. Heat treatment for these samples was carried out in a circulating nitrogen chamber at 230°C for two hours, and then at 270°C for 16 hours. In the machine direction (M.D.), the effect of heat treatment on the tensile strength of the extruded sheets was greater in HNA/TA/AAA polymer than in HBA/HNA polymer. This may be due to the former polymer having a greater tendency to form an anisotropic melt during the extrusion. There was no significant improvement in the mechanical properties for both polymers in the transverse direction. The ultimate elongation was increased by the heat treatment, while modulus decreased. These phenomena are

1/4" Extruded Rod (Dr = 1~1.2)

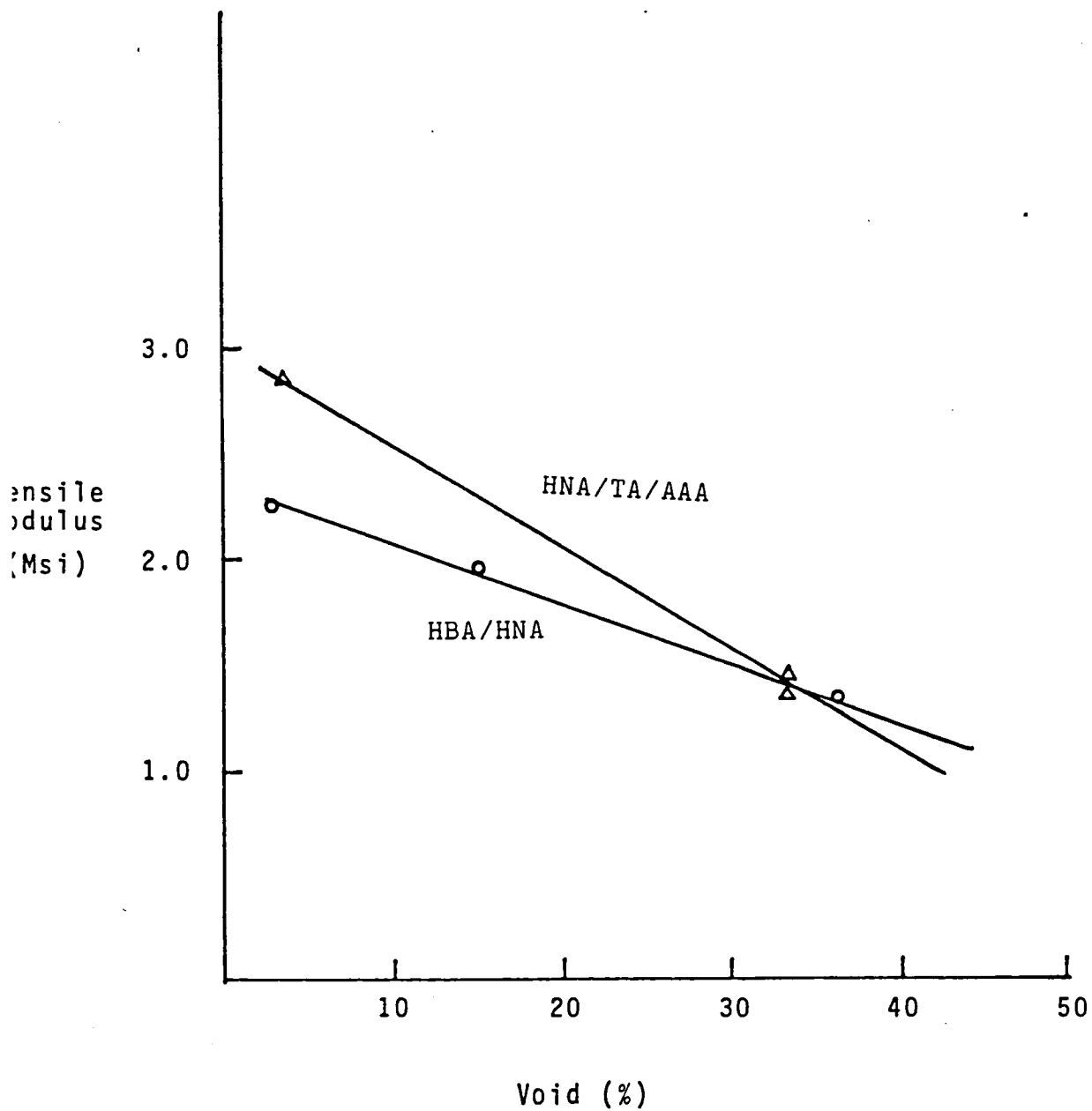
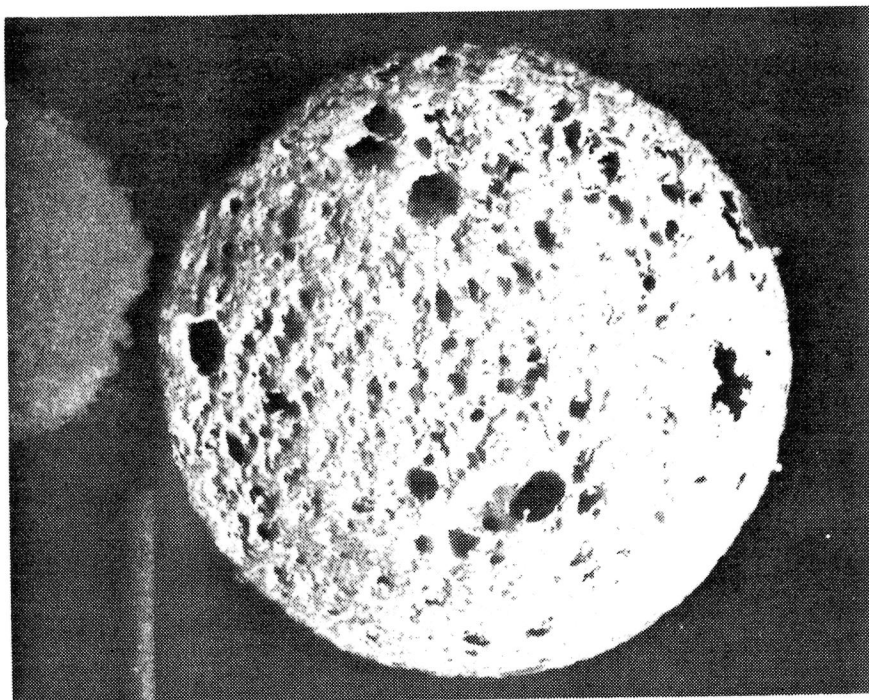
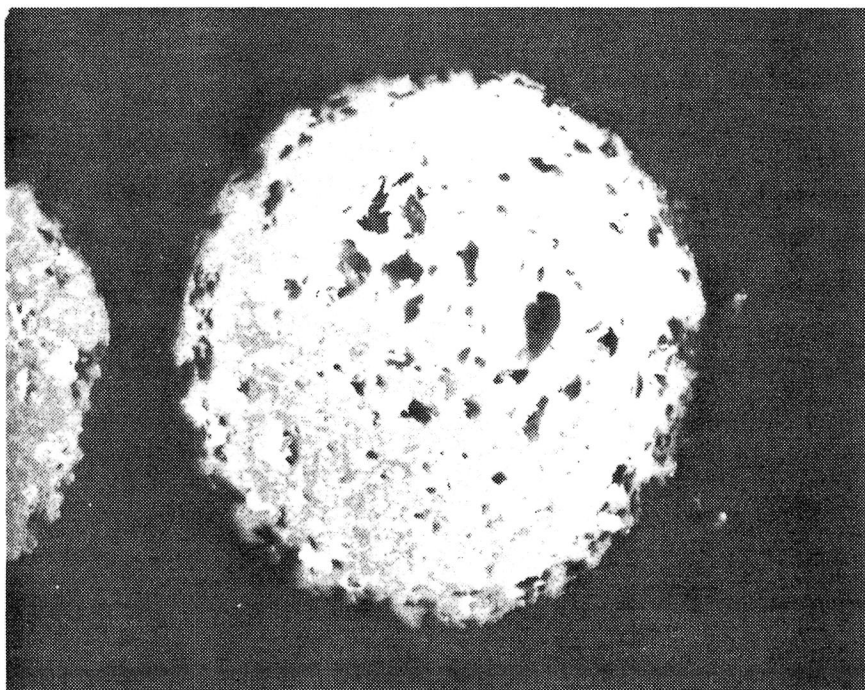


FIGURE 4. TENSILE MODULI OF RODS AS A FUNCTION OF VOID CONTENT



HNA/TA/AAA + 30% Glass Rod



HBA/HNA + 30% Glass Rod

FIGURE 5. MORPHOLOGY OF THE FOAM RODS

TABLE 3. ORIENTATION ANGLE AND HERMAN'S FUNCTION OF
LIQUID CRYSTAL POLYMER FOAM

<u>Material</u>	<u>Void %</u>	<u>Orientation Angle <110></u>	<u>Herman's Function</u>
HBA/HNA	4	19.29	.8304
	34	20.09	.6764
HNA/TA/AAA	8.3	23.39	0.7908
	33	26.71	0.7118

42 Mil Sheet ($D_R = 2$)

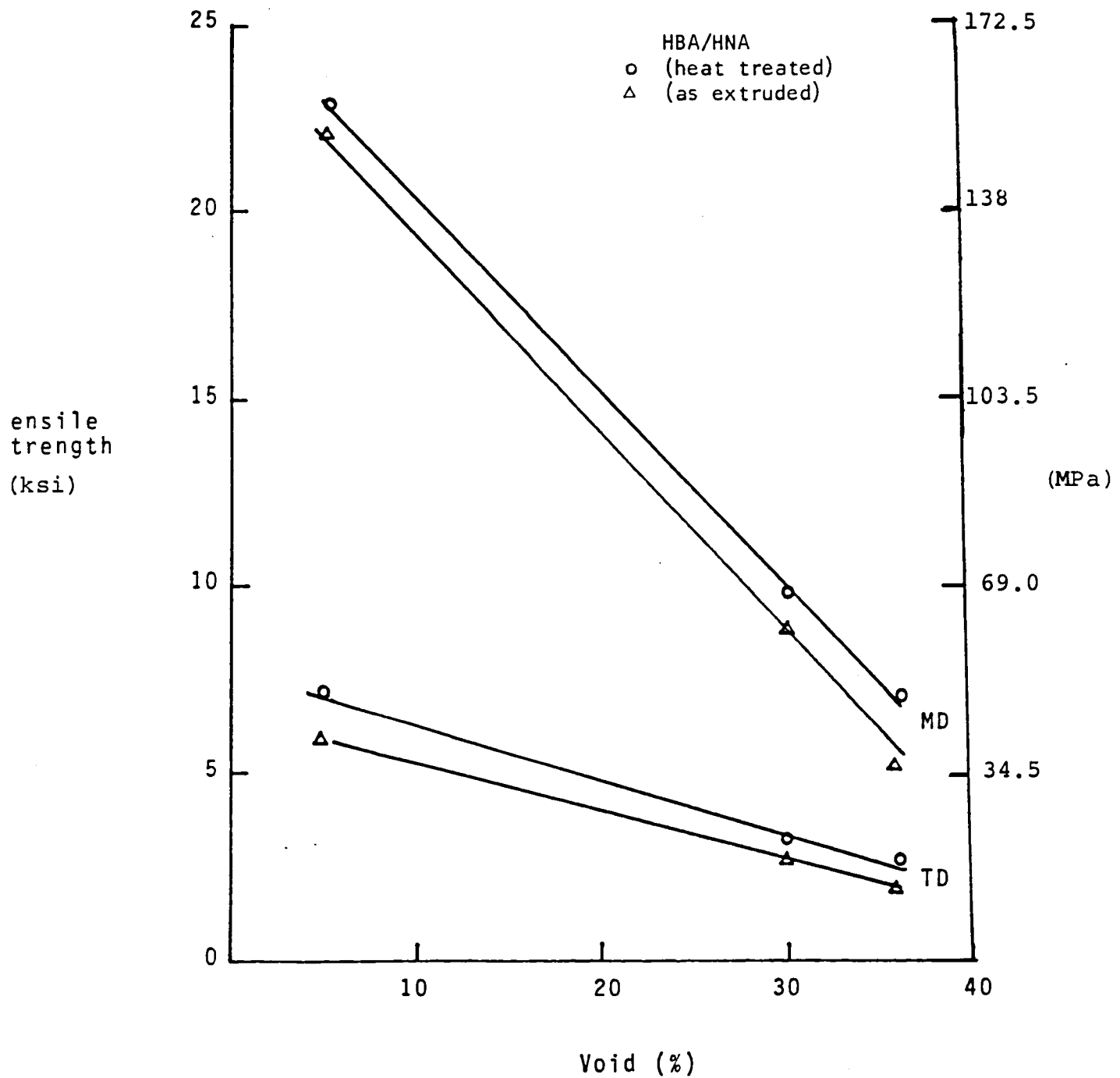


FIGURE 6. TENSILE STRENGTH OF HBA/HNA SHEET FOAMS

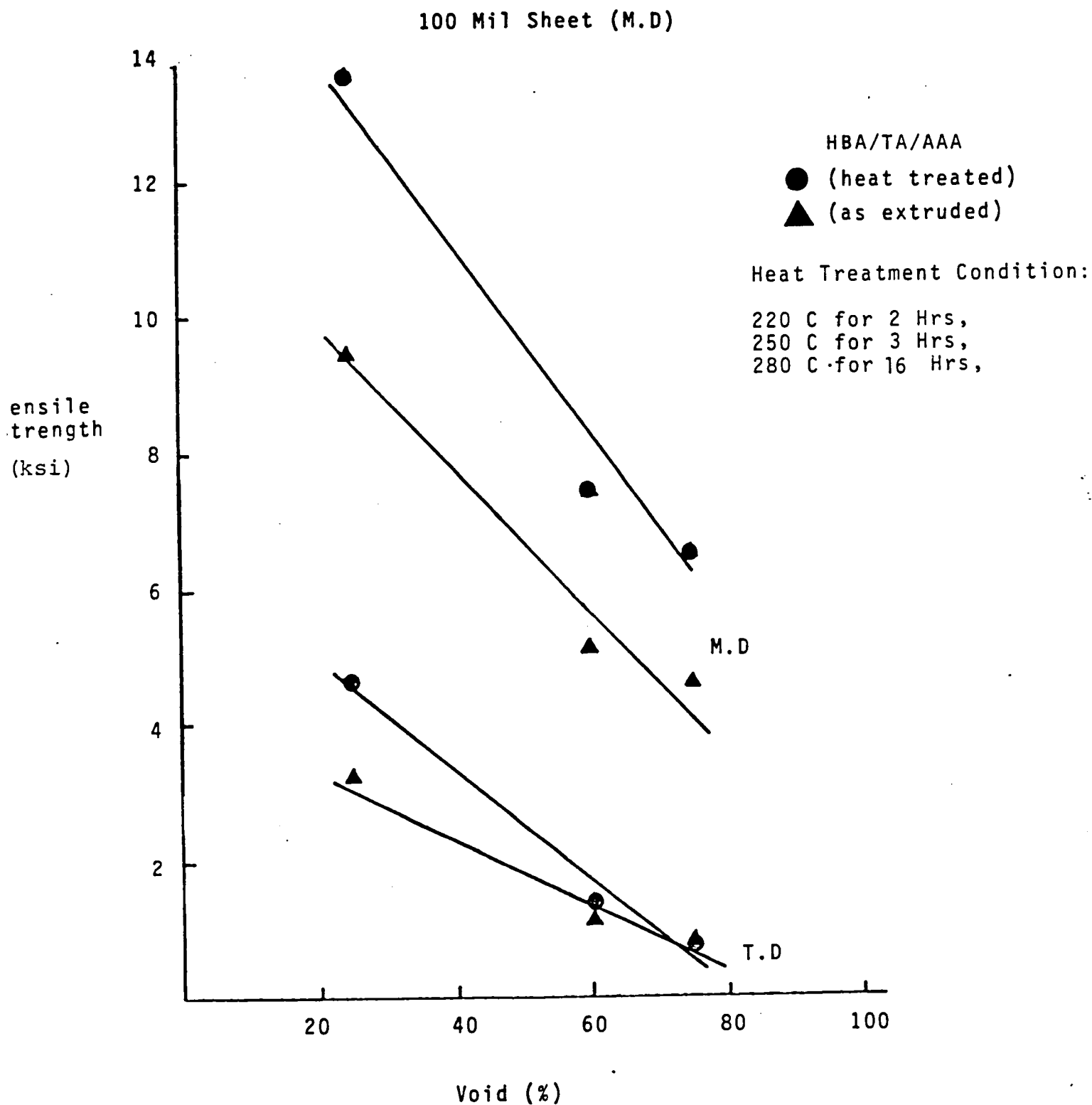


FIGURE 7. TENSILE STRENGTH OF HNA/TA/AAA SHEET FOAMS

TABLE 4A. TENSILE PROPERTIES OF HBA/HNA 73/27 EXTRUDED SHEET IN THE MACHINE DIRECTION⁽¹⁾

	Void Content (%)	AS EXTRUDED				HEAT TREATED			
		<u>Strength/Elongation/Modulus</u>				<u>Strength/Elongation/Modulus</u>			
		<u>MPa / % / GPA</u>		<u>Ksi / % / Msi</u>		<u>MPa / % / GPA</u>		<u>Ksi / % / Msi</u>	
HBA/HNA 73/27	4.9	153/1.86/12.3		22.2/1.86/1.79		151.7/2.4/8.9		22.8/2.4/1.29	
HBA/HNA 73/27 .1% Kemtec 1% Wollastonite	29.9	61.7/2.13/4.75		8.94/2.13/0.69		67.7/2.9/4.1		9.81/2.9/0.59	
HBA/HNA 73/27 .1% Celogen 1% Wollastonite	35.9	35.4/2.89/2.3		5.13/2.89/0.33		51.7/4.5/2.7		7.5/4.5/0.39	

(1) Extruded with a 10.16 cm (4 in) wide tape die. The extrusion speed was 7.62 cm/min (3 in/min).

TABLE 4B. TENSILE PROPERTIES OF EXTRUDED HBA/HNA 73/27 SHEET IN THE TRANSVERSE DIRECTION⁽¹⁾

	Void Content (%)	AS EXTRUDED		HEAT TREATED	
		Strength/Elongation/Modulus		Strength/Elongation/Modulus	
		MPa / % / GPA	Ksi / % / Msi	MPa / % / GPA	Ksi / % / Msi
HBA/HNA 73/27	4.9	40.9/4.3/2	5.93/4.3/.29	49.0/5.9/2.41	7.1/5.9/0.35
HBA/HNA 73/27 .1% Kemtec 1% Wollastonite	29.9	18.1/3.1/1.38	2.63/3.1/.20	23.4/4.2/1.45	3.4/4.2/.21
HBA/HNA 73/27 .1% Celogen 1% Wollastonite	35.9	15.2/3.19/1.2	2.2/3.19/.17	19.6/5.0/1.29	2.84/5.0/.187

TABLE 5A. TENSILE PROPERTIES OF HNA/TA/AAA (60/20/20) EXTRUDED SHEET^{(1) (2)}
IN THE MACHINE DIRECTION

Void Content (%)	AS EXTRUDED		HEAT TREATED	
	<u>Strength/Elongation/Modulus</u>		<u>Strength/Elongation/Modulus</u>	
	<u>MPa / % / GPa</u>	<u>Ksi / % / Msi</u>	<u>MPa / % / GPa</u>	<u>Ksi / % / Msi</u>
25	67.0/0.93/8.38	9.59/.93/1.19	95.0/1.56/9.92	13.6/1.56/1.42
59	36.3/0.82/5.24	5.20/0.82/0.75	51.8/1.11/5.52	7.42/1.11/ .79
74	33.0/0.72/5.45	4.72/0.72/0.78	46.3/1.04/5.24	6.62/1.04/ .75

TABLE 5B. TENSILE PROPERTIES OF HNA/TA/AAA (60/20/20) EXTRUDED SHEET^{(1) (2)}
IN THE TRANSVERSE DIRECTION

Void Content (%)	AS EXTRUDED		HEAT TREATED	
	<u>Strength/Elongation/Modulus</u>		<u>Strength/Elongation/Modulus</u>	
	<u>MPa / % / GPa</u>	<u>Ksi / % / Msi</u>	<u>MPa / % / GPa</u>	<u>Ksi / % / Msi</u>
25	23.4/1.06/2.64	3.35/1.06/0.36	27.1/1.00/3.84	3.88/1.00/0.55
59	8.52/1.15/1.17	1.16/1.15/0.164	9.36/1.85/1.02	1.34/1.85/0.146
74	6.24/1.11/1.03	0.85/1.11/0.140	4.68/1.10/0.73	0.67/1.10/0.105

(1) Extruded with a 10.16 cm (4") wide tape die. The extrusion speed was 7.62 cm/min (3"/min). Draw-down ratio = 1.7-2.0.

(2) Polymer contained 0.3% Celogen and 1% Wollastonite.

clearly attributable to the relaxation of the liquid crystal polymer during the heat treatment.

The tensile property retention in the machine direction was poorer than in the transverse direction. This is because bubbles affect molecules oriented in the machined direction more than the molecules oriented in the transverse direction.

Experimental experience also indicated that HNA/TA/AAA polymer had a better melt strength (elongation-thickening character) than HBA/HNA polymer. As a result, the former could partially hold the bubbles created by the chemical blowing agents, while the latter had a visible irregular structure on the surface of extruded sheets. In addition, due to these rheological differences, high void content (>70%) foams could only be prepared with HNA/TA/AAA polymer.

2. Injection Molded Foams:

a. Foams Made by the Conventional Injection Molding Process: Tables 6 and 7 give the mechanical properties of injection molded HBA/HNA (73/27) and HNA/TA/AAA (60/20/20) samples, respectively. Both the tensile and flexural property retentions of HBA/HNA samples are superior to those of HNA/TA/AAA samples. This is because the effect of voids on molecular disorientation is smaller in the former than in the latter. In order to compare the mechanical property retention of both polymers to those of conventional polymers, we have plotted the mechanical properties of LCP foams versus the theoretical predictions calculated using Equations 7 and 9 for tensile strength and flexural modulus, respectively. Figures 8 and 9 demonstrate the results and show that both HBA/HNA (73/27) and HNA/TA/AAA (60/20/20) have better flexural modulus retention than those predicated by the empirical equations. However, only HBA/HNA (73/27) has superior tensile

TABLE 6. MECHANICAL PROPERTIES OF CONVENTIONAL INJECTION-MOLDED HBA/HNA (73/27)⁽¹⁾
1/4"THICK BAR

Void (%)	Tensile		Flexural	
	Strength/Elongation/Modulus		Strength/Modulus	
	MPa / % / GPa	Ksi / % / Msi	MPa / GPa	Ksi / Msi
0	111.1/3.94/5.6	15.9/3.94/0.80	121.6/0.88	17.4/0.88
7.5	86.6/2.48/5.9	12.4/2.48/0.85		
27.1	83.1/2.31/5.8	11.9/2.31/0.83	64.5/0.59	11.5/0.68
38.0	69.2/2.7 /4.6	9.9/2.7 /0.66		
43.0	/4.5	/0.65	69.5/0.75	9.94/0.75

TABLE 7. MECHANICAL PROPERTIES OF CONVENTIONAL INJECTION-MOLDED HNA/TA/AAA⁽¹⁾
(60/20/20) 1/4"THICK BAR

Void (%)	Tensile		Flexural	
	Strength/Elongation/Modulus		Strength/Modulus	
	MPa / % / GPa	Ksi / % / Msi	MPa / GPa	Ksi / Msi
0	113.9/1.0/12.9	16.3/1.0/1.84	183.1/13.3	26.2/1.91
8	93.0/1.07/10.1	13.1/1.07/1.45	127.2/10.7	18.2/1.53
27	39.8/0.61/7.0	5.7/0.61/1.00	101.3/9.2	14.5/1.31
50	/5.1	/0.73	73.4/6.7	10.5/0.96

(1) With 1% Wollastonite and 0.3% Celogen by weight.

1/4" Thick Injection Molded Part

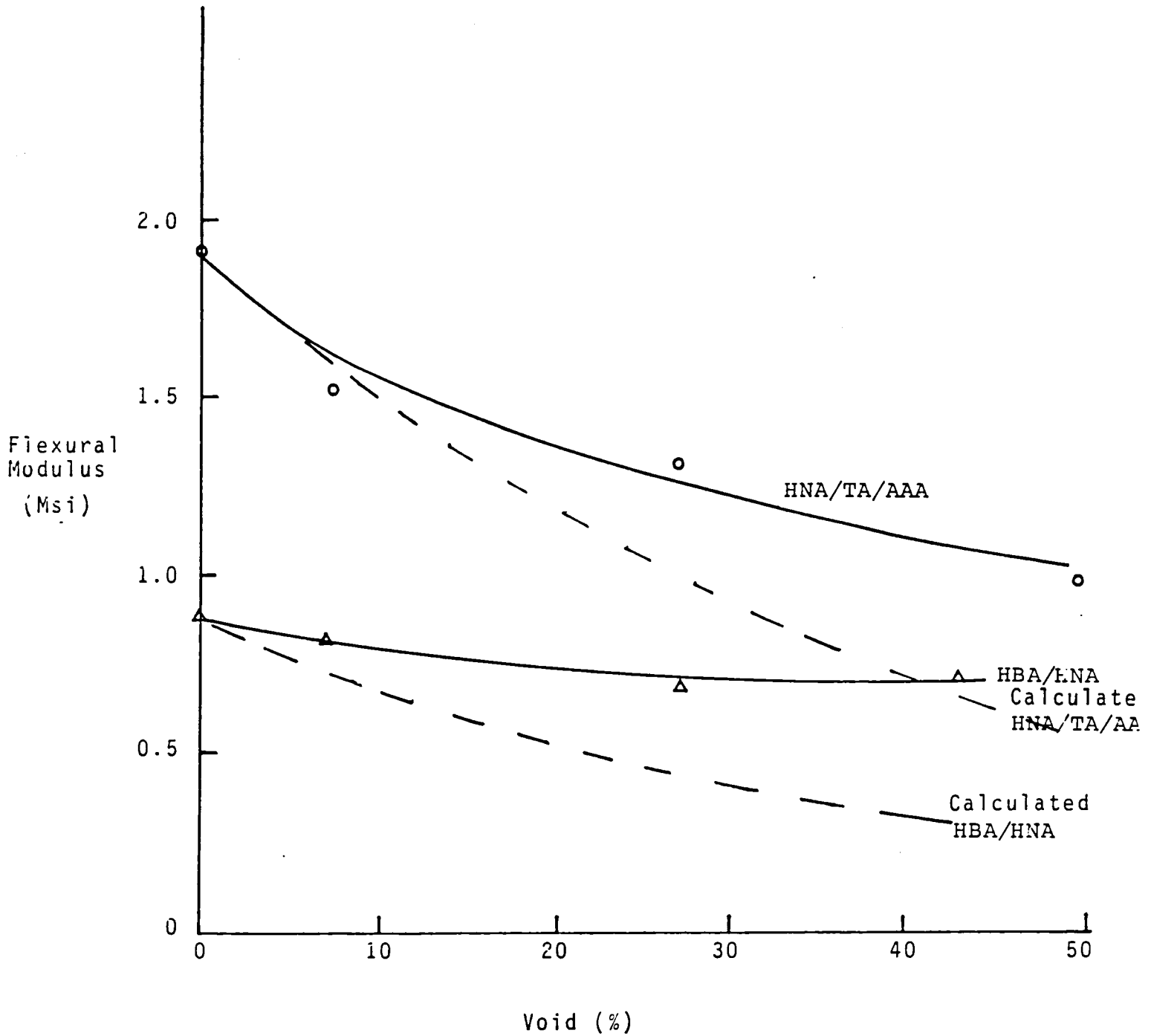


FIGURE 8. FLEXURAL MODULUS OF 1/4" THICK CONVENTIONAL INJECTION-MOLDED FOAMS

1/4" Thick Injection Molded Sample

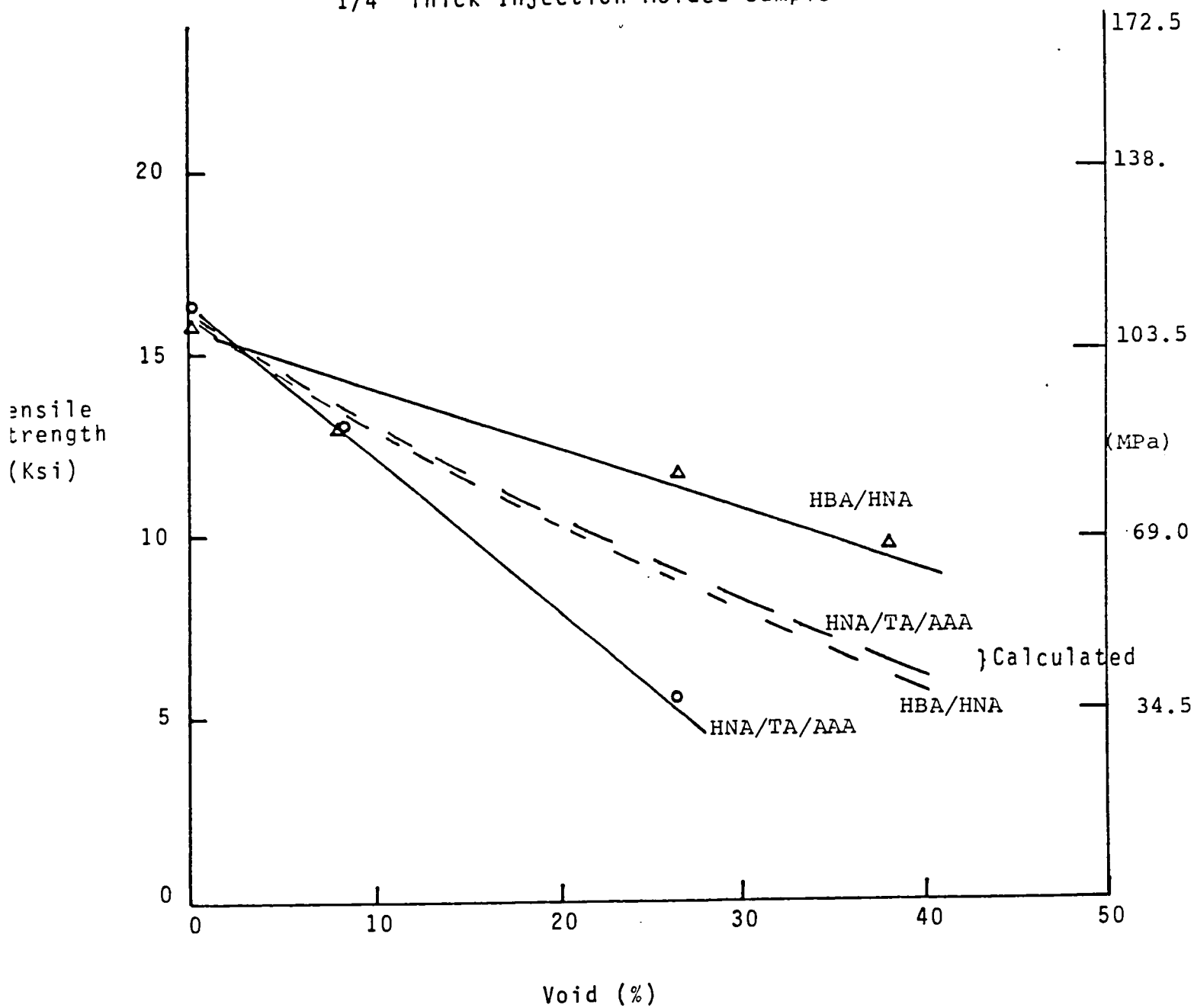


FIGURE 9. TENSILE STRENGTH OF 1/4" THICK CONVENTIONAL INJECTION-MOLDED FOAMS

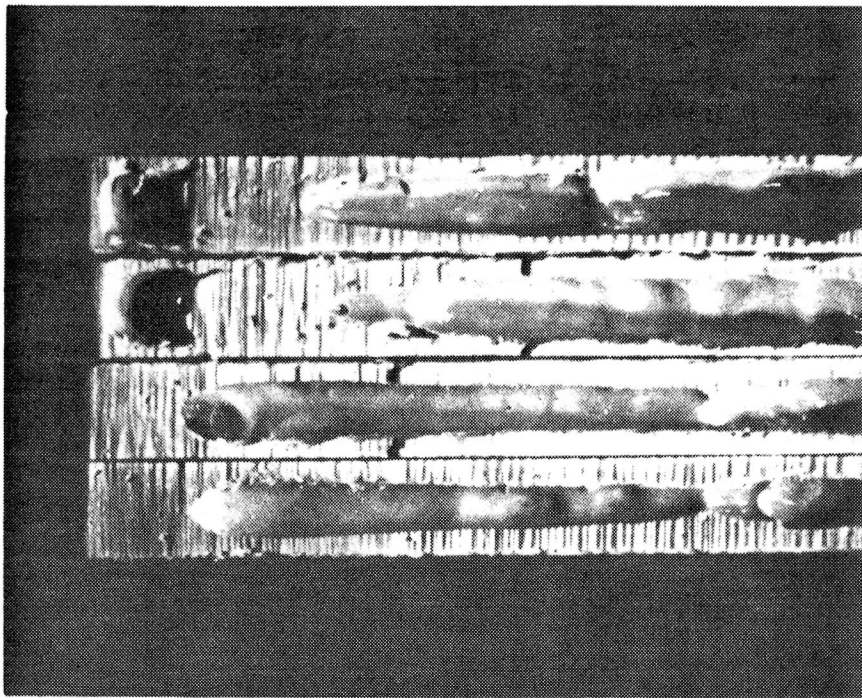
strength retention. The skin-core structure of HBA/HNA (73/27) foam is shown in Figure 10, and the void distribution is poor. This may be due to the fact that both polymers have significantly lower viscosity as well as longer relaxation time than the conventional polymers. In addition, this may also be due to the fact that the melt residence time in the injection barrel was too short to mix uniformly with bubbles. Therefore, although the molded LCP foams have good mechanical properties, the reliability of this process is uncertain.

Table 8 summarizes the mechanical properties of 0.3175 cm (1/8") thick injection molded foams. Data reconfirm that HBA/HNA polymer foam has better tensile and flexural property retention than that of HNA/TA/AAA polymer foam. However, both polymers have poor Izod impact and heat-deflection temperature retention. These poor retentions result from the distinct skin-core structure of liquid crystal polymer foams.

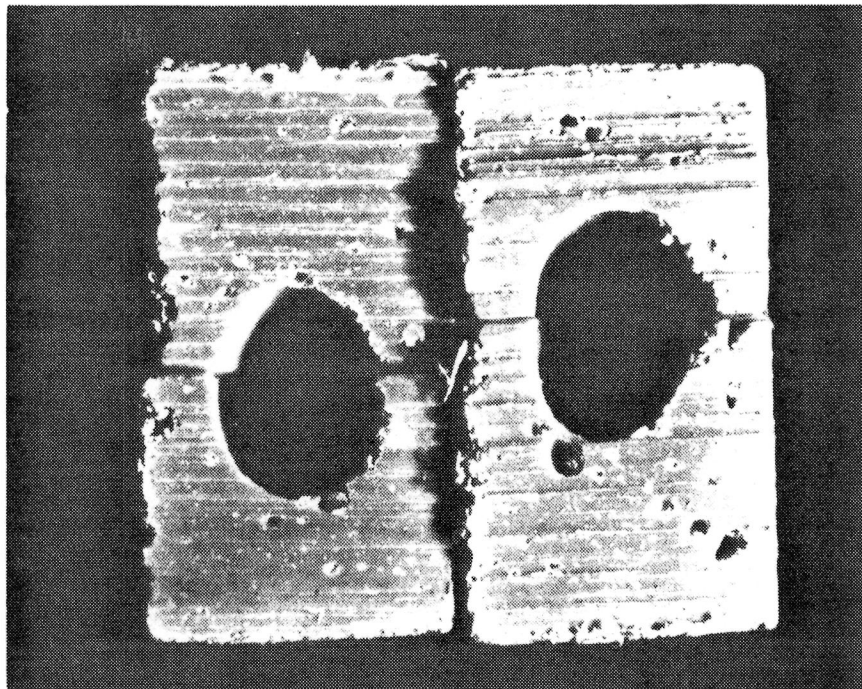
Tables 9A and 9B summarize the mechanical properties for the glass fiber reinforced LCP foam-molded bars. Both polymers have poor mechanical property retention (except for retention of flexural properties of HBA/HNA). A likely reason for this is that the highly oriented glass fibers disorient due to void formation. In addition, since glass fibers provided the nucleation sites for bubble growth (4-6), existence of gas bubbles may destroy the interfacial adhesion between the fibers and liquid crystal polymers.

b. Foams Made by a Union-Carbide Low-Pressure Process:

Mechanical properties of 0.635 cm (1/4") ram injection molded foams are summarized in Table 10, and show that the overall mechanical properties of foams are inferior to those foams made by the conventional reciprocating screw injection-molding machine. This is due to the conventional injection process using higher pressure and faster injection speed than the Union-Carbide



a. Cross Section in the Machine Direction



b. Cross Section in the Thickness Direction

FIGURE 10. OPTICAL MICROGRAPHS OF LCP MOLDED BAR MADE BY A CONVENTIONAL MOLDING MACHINE

TABLE 8. MECHANICAL PROPERTIES OF INJECTION-MOLDED 1/8" THICK FOAMS

<u>Material</u>	<u>Void (%)</u>	<u>Tensile Strength</u>		<u>Flexural Strength</u>		<u>Izod Impact</u>		<u>Heat-Deflection</u>
		<u>Elongation/Modulus</u>		<u>Modulus</u>		<u>J/m (ft-lb/in)</u>		<u>Temperature</u>
		<u>MPa/%/GPa</u>	<u>(Ksi/%/Msi)</u>	<u>MPaGPa</u>	<u>(Ksi/Msi)</u>	<u>Notch</u>		<u>°C</u>
HBA/HNA	0	168/1.4/21.0	24/1.4/3	167/9.3	24/1.3	427	8	180
	8.5			126/8.2	18/1.18	213	4	157
	20	148/1.39/20.3	21.2/1.39/2.9					
HNA/TA/AAA	0	182/1/20.3	26/1/2.9	258/16.3	37/2.3	427	8	195
	6.5					115	2.15	169
	8.5			168/13.3	24/1.9			
	19	154/1.12/16.8	22/1.12/2.4					

TABLE 9A. MECHANICAL PROPERTIES OF 30% GLASS FIBER REINFORCED HBA/HNA (73/27)⁽¹⁾
1/4" CONVENTIONAL INJECTION-MOLDED BAR

Void (%)	Tensile		Flexural	
	Strength/Elongation/Modulus		Strength/Modulus	
	MPa / % / GPa	Ksi / % / Msi	MPa / GPa	Ksi / Msi
0	163.2/2.77/12.5	23.6/2.77/1.79	204.7/11.7	29.3/1.68
9.8	89.4/1.68/8.6	12.8/1.68/1.23	170 /10.1	24.3/1.45
10.7	82.8/1.51/8.4	11.85/1.51/1.20	170 /10.0	24.3/1.43

TABLE 9B. MECHANICAL PROPERTIES OF 30% GLASS FIBER REINFORCED HNA/TA/AAA⁽¹⁾
(60/20/20) 1/4" CONVENTIONAL INJECTION-MOLDED BAR

Void (%)	Tensile		Flexural	
	Strength/Elongation/Modulus		Strength/Modulus	
	MPa / % / GPa	Ksi / % / Msi	MPa / GPa	Ksi / Msi
0	171.9/1.07/19.6	24.6/1.07/2.81	249.4/18.3	35.7/2.62
25.2	88.7/0.78/13.6	12.7/0.78/1.45	111.8/10.4	16.0/1.58
29.4	42.5/0.58/7.8	6.08/0.58/1.12	117.4/10.7	16.8/1.53

(1) With 1% Wollastonite and 0.3% Celogen by weight.

TABLE 10. MECHANICAL PROPERTIES OF 1/4" RAM INJECTION-MOLDED FOAMS

M.D.	Void (%)	Tensile Str/Elongation/Modulus MPa / % / GPa Ksi / % / Msi		(1) Flexural Strength/Modulus MPa/GPa Ksi/Msi		(2) Izod Impact J/M(ft-lbs/in-) Notch		Heat-Deflection Temperature °C
HBA/HNA	7.2	69.6/3.7/3.93	10.1/3.7/0.57			161.2	3.02	
	19	46.6/3.6/2.76	6.75/3.6/0.40			143.6	2.69	
	34.5	23.0/3.2/1.59	3.36/3.2/0.23			46.4	0.87	
	37					34.2	0.64	
T.D.	7.2	49.0/4.1/2.83	7.10/4.1/0.41	60.4/2.21	8.76/0.32	252.	4.72	95
	15	33.2/2.8/2.27	4.82/2.8/0.33	50.9/1.86	7.38/0.27	216.	4.04	86
	33	20.3/2.58/1.45	2.95/2.58/0.21	36.8/1.52	5.34/0.22	90.2	1.69	69
	37					149.	2.77	60

(1) Tested at 5% strain.

(2) Notch direction is the test direction.

conventional molding process is much smaller than that of the low-pressure process (0.635 cm vs. 2.54 cm), parts fabricated by the former process have greater orientation than those produced by the low-pressure ram injection-molding process.

Figure 11 illustrates variation in the foam modulus with void content. The dotted line was calculated using Equation 9. Flexural modulus retentions in the transverse direction follow the trend of the conventional polymeric foams, while Figure 12 shows that the tensile property retentions in both directions are slightly below the calculations. Since the liquid crystal polymer in the transverse direction is not highly oriented, it is reasonable that their flexural and tensile modulus retentions behave close to those of conventional polymeric foams. On the other hand, liquid crystal polymers in the machine direction lose orientation significantly due to the bubble formation; and their tensile strength and modulus retentions are, therefore, slightly poorer than those in the transverse direction. In addition, since there is no distinct skin-core structure in this type of foam (as shown in Figure 13), their mechanical property retention is well below that of foams made by the conventional reciprocating screw injection-molding process.

Table 10 gives the Izod impact strength of liquid crystal polymer foams as a function of void content and test direction. Foams have higher impact properties if the notch impact was taken perpendicularly to the flow direction (or machine direction) than to the transverse direction. This difference is due to oriented liquid crystal polymers having poor intermolecular cohesion. As a result, cracks propagate faster in the flow direction than in the transverse direction. The effect of void content on the heat-deflection temperature is also shown in Table 10. It indicates that an increase in void content results in a decrease in the heat-deflection temperature. Table 11 summarizes the effect of void content on the foam coefficient of thermal expansion

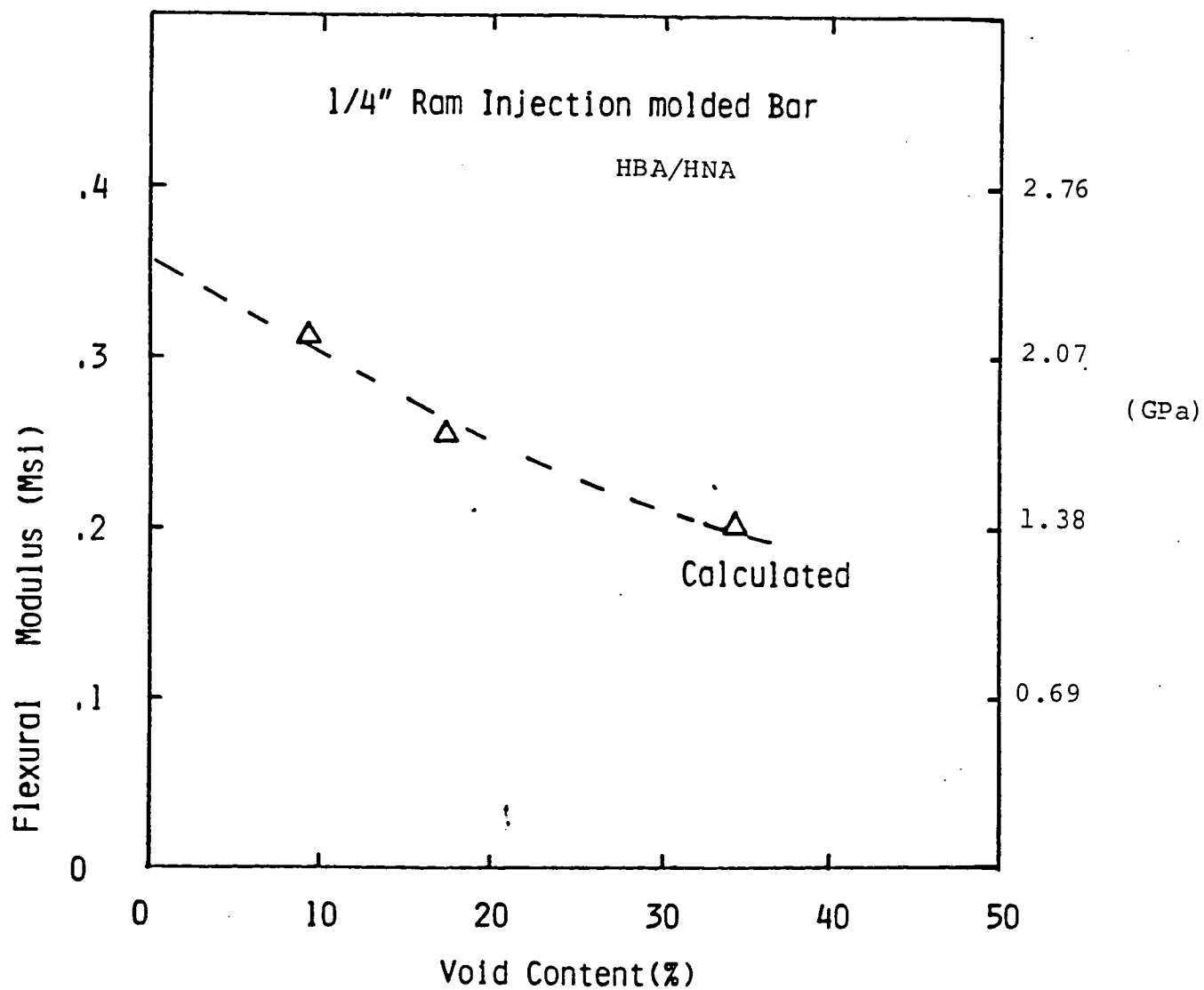


FIGURE 11. FLEXURAL MODULUS OF LCP FOAMS AS A FUNCTION OF VOID CONTENT

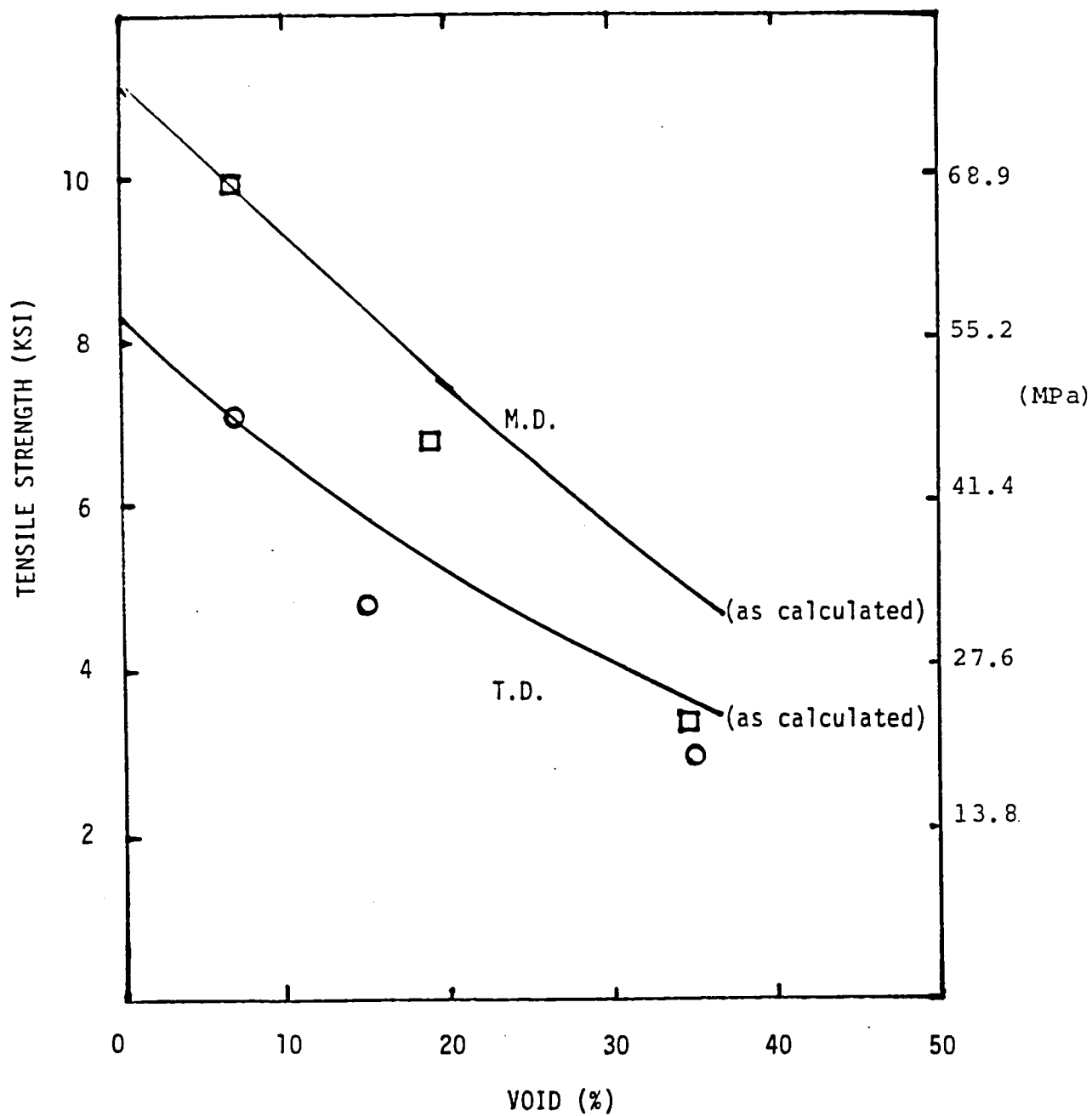
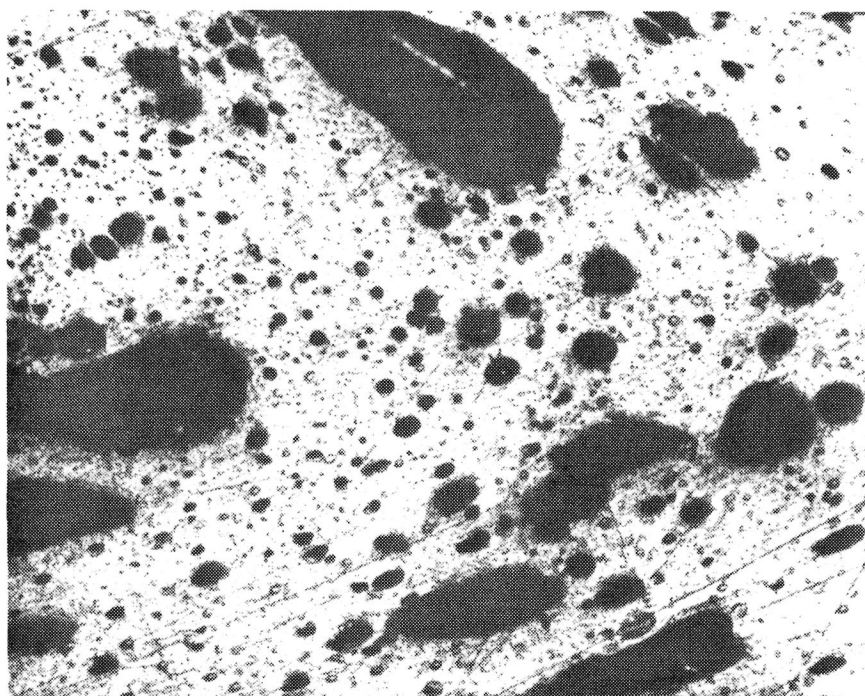


FIGURE 12. TENSILE PROPERTIES AS A FUNCTION OF VOID CONTENT FOR RAM INJECTION-MOLDED 1/4" HBA/HNA FOAM



(X50)

FIGURE 13. OPTICAL MICROGRAPHS OF RAM INJECTION-MOLDED
HBA/HNA FOAMS

TABLE 11. THERMAL EXPANSION COEFFICIENT OF LCP FOAMS MADE
BY A RAM INJECTION-MOLDING MACHINE

Void (%)	CTE (10^{-5} x in/in °C)		
	M.D.	T.D.	Thickness Direction
7.5	2.8	6.1	20.2
15	2.1	7.6	14.3
35	5.2	9.2	13.1

TABLE 12. IMPACT PROPERTIES OF 1/4" THICK INJECTION-MOLDED FOAMS

Void %	Max. Load		Spec. Load ⁽¹⁾ Newton	Energy at Max. Load		Spec. Energy ⁽²⁾ J	Total Energy	
	Newton (16)			J	(Ft-lb)		J	(Ft-lb)
4.8	4484	1008	4710	9.21	6.79	9.67	33.6	24.81
13.1	4101	922	4714	7.99	5.89	9.19	18.8	13.9
28.2	3025	680	4213	6.56	4.84	9.13	17.2	12.7
37.8	2775	624	4418	5.46	4.03	8.78	17.7	13.1

(1) Specific load is defined as maximum load/(1-void content)

(2) Specific energy is defined as energy at maximum load/(1-void content)

expansion (CTE), and shows that the CTE is highest in the thickness direction and lowest in the machine direction. However, they tend to become close to one another as the void content increases. This indicates that the anisotropic character of LCP moldings is reduced with increasing void content.

3. Comparison Between Liquid Crystal Polymeric Foam and the Conventional Foams:

A comparison between LCP foams and the conventional plastic foams is summarized in Table 13. Since the conventional injection-molding process does not give uniform void distribution, only foams made by a ram injection-molding process (Union-Carbide low-pressure process) are considered in this table. The first two columns show the mechanical properties of LCP foams, and the rest list the properties of Polycarbonate, PBT, ABS, and Polystyrene. Although their void contents are different, the following conclusion may be drawn from this table.

LCP foams have better properties than those of ABS and Polystyrene. However, their properties are only comparable to PBT foams and inferior to Polycarbonate foams. LCP foams have poor heat-deflection temperature, as well as impact resistance energy. Thermal expansion coefficient results also indicated that LCP foams with 33% voids are still anisotropic.

These deficiencies arise from the fact that LCP molecules had not been fully oriented during the Union-Carbide low-pressure process. In other words, because the Union-Carbide process used a low injection pressure, a slow injection speed, and a large diameter runner, the driving force to oriented LCP molecules is significantly small compared to the in-house injection-molding process. As a result, both tensile and flexural properties of LCP foams are inferior to the Polycarbonate foams. Similarly, the remarkable drop in the heat-deflection temperature is also due to the lack of orientation.

TABLE 13. COMPARISON OF LCP HBA/HNA FOAMS WITH CONVENTIONAL FOAMS

<u>Properties</u>	<u>LCP HBA/HNA</u>				<u>Polycarbonate</u>	<u>PBT</u>	<u>ABS</u>		<u>Poly-styrene</u>
	M.D.		T.D.		(Lexan) ⁽²⁾	(Valox) ⁽¹⁾	(Cyclon	FBK) ⁽²⁾	(Furid) ⁽²⁾
Void %	16-17	33-35	16-17	33-35	26	23	20	30	24
Tensile ⁽⁵⁾ Strength (Ksi)	6.75	3.4	4.8	3.0	6.1	3.4	1.9	X	.20
Tensile Mod- ulus (Msi)	0.4	0.73	0.32	0.21	0.3	0.23	0.16	X	0.23
Elongation (%)	3.6	3.23	2.7	2.6	4.6	6.0	X	X	2.4
Flexural Strength (Ksi)	(3) X	X	7.4	5.3	11.6	6.8	6.0	4.2	4.6
45 Flexural Modulus (Msi)	X	X	0.27	0.22	0.35	0.26	0.24	0.22	0.27
Heat Deflec- tion Temper- ature (°C)	X	X	86	69	127	82	70	65	69
Thermal Expansion Coefficient (L/W/T) (10 ⁻⁵ in/in-°C)	5.2/9.2/13.1 ⁽⁴⁾					3.6			
Impact Energy (ft-lb) ⁽⁶⁾	13.1 ⁽⁴⁾				35	12	10<		8-10

1) Trade name of Gen. Electrical Chemical Co. Data copied from their technical brochure.

2) Trade names of Borg Warner Chemical Co. Data copied from their technical brochure.

3) Denotes no data available.

4) LCP foams with 34% void.

5) 1 Ksi = 6.897 MPa.

6) 1 ft-lb = 1.3558 Joules.

In addition, since LCP has weak intermolecular cohesion, strong anisotropic character, and low elongation-to-break, LCP foams have difficulty uniformly dissipating the external force during the impact tests. Therefore, they have less crack resistance than the Polycarbonate foams.

4. Potential Applications of LCP Foams:

Applications of structural foams may be divided into 12 different market segments. Table 14 shows the market segment estimates and the polymers which are used for structural foam in these applications¹. Except for Polycarbonate foams, LCP foams may have the potential to replace the others. However, since LCP's are more expensive than those conventional polymers, potential applications of LCP foams in these areas are quite limited.

Conversely, LCP's have very good chemical resistance which no conventional polymers have. There is the possibility of using LCP foams in the area of military and severe chemical environments.

VI. CONCLUSIONS

The following conclusions can be drawn from this study:

(A) Extrusion Foams:

1. Extruded HNA/TA/AAA foams have better quality and appearance than HBA/HNA foams, though the former has less mechanical property retention than the latter.
2. Heat treatment increases extruded foam tensile strength and elongation, but reduces the tensile modulus.

TABLE 14. STRUCTURAL FOAM CONSUMPTION BY POLYMER AND
MARKET SEGMENT (Million Pounds)⁽¹⁾

	PC	PPO	PEST	ABS	PS	PP	PE	PU	PVC	SMA	Totals
Appliances	small			1	3	small					4
Building and Construction					25	5	1	3	29		63
Business Machines	9	41	1	1	6			4			62
Consumer Electronics	small	small		3	5	small					8
Furniture				1	12	11	1	20			45
Maintenance/Waste Containers						3	25				28
Materials Handling	small				2	7	36				45
Medical/analytical	1	1	small		small			1			3
Recreation				6	10	3	2	3			24
Tools	1			small	3	3					7
Transportation	2	small	1	3	small	4	6			2	18
Utility Enclosure/Conduit				3	7	4	46				60
Miscellaneous	1	small		small	15	2	9	small			27
Totals	14	42	2	18	88	42	126	31	29	2	394

(1) Data obtained from Reference 1

(B) Injection-Molded Foams:

1. Nitrogen foaming agent with a low-pressure process gives better void distribution in injection-molded LCP foams than does conventional injection molding process with chemical blowing agents.
2. The flexural modulus of injection molded HBA/HNA foams follows the empirical equation for conventional polymeric foams. However, their tensile properties are slightly lower than the predictions. LCP (HBA/HNA) foams have better mechanical properties than foamed ABS and PS, but are comparable to PBT and inferior to Polycarbonate foams.
3. Glass fibers have negative effects on foam mechanical properties.
4. No applications have been identified to date. However, LCP foams should have potential in applications requiring chemical resistance and low part weight as primary performance criteria.

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16. Abstract Two types of liquid crystal polymer (LCP) compositions were studied and evaluated as structural foam materials. One is a copolymer of 6-hydroxy-2-naphthoic acid, terephthalic acid, and p-acetoxycetanilide (designated HNA/TA/AAA), and the other is a copolymer of p-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid (designated HBA/HNA). Experimental results showed that the extruded HNA/TA/AAA foams have better mechanical quality and appearance than HBA/HNA foams. Heat treatment improved foam tensile strength and break elongation, but reduced their modulus. The injection molding results indicated that nitrogen foaming agents with a low-pressure process gave better void distribution in the injection molded LCP foams than those made by the conventional injection-molding machine and chemical blowing agents. However, in comparing LCP foams with other conventional plastic foams, HBA/HNA foams have better mechanical properties than foamed ABS and PS, but are comparable to PBT and inferior to polycarbonate foams, especially in heat-deflection temperature and impact resistance energy. These deficiencies are due to LCP molecules not having been fully oriented during the Union-Carbide low-pressure foaming process.					
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